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A research program to study the oxidation and ignition chemistry of single and multiple component hydrocarbon fuels at high pressures has been conducted at Drexel University. The current program was initiated in May 1998 through a grant from the Army Research Office (Grant No. DAAG55-98-1-0286, Project No. 37699-EG) and was completed in April 2002. The program was augmented by efforts under an associated AASERT award (Grant No. DAAG55-97-1-0196; Project No. 36910-EG-AAS). The purpose of this project was to investigate the complex interactions between individual components of 2, 3, and 4 component mixtures and full boiling range fuels by developing kinetic and mechanistic information in the low and intermediate temperature ranges (600 – 1000 K) and at elevated pressures (up to 20 atm). In addition, simplified blends were developed to mimic the behavior of gasoline and JP-8 distillate fuels in the low and intermediate temperature regime.

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AND THEIR MIXTURES AT HIGH PRESSURE

FINAL REPORT

N.P. Cernansky and D.L. Miller

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## ABSTRACT

A research program to study the oxidation and ignition chemistry of single and multiple component hydrocarbon fuels at high pressures has been conducted at Drexel University. The current program was initiated in May 1998 through a grant from the Army Research Office (Grant No. DAAG55-98-1-0286, Project No. 37699-EG) and was completed in April 2002. The program was augmented by efforts under an associated AASERT award (Grant No. DAAG55-97-1-0196; Project No. 36910-EG-AAS). The purpose of this project was to investigate the complex interactions between individual components of 2, 3, and 4 component mixtures and full boiling range fuels by developing kinetic and mechanistic information in the low and intermediate temperature ranges (600 – 1000 K) and at elevated pressures (up to 20 atm). In addition, simplified blends were developed to mimic the behavior of gasoline and JP-8 distillate fuels in the low and intermediate temperature regime.

Each fuel examined was partially oxidized in the Drexel Pressurized Flow Reactor (PFR) facility. This facility allows for well controlled and repeatable experiments to be conducted at various pressures, temperatures, and reaction times. Generally, two types of experiments were conducted for each fuel, Controlled Cool Down (CCD) and Constant Inlet Temperature (CIT). The CCD experiment generates a CO reactivity map and the behavior of intermediate species over a range of temperatures, nominally 800 K to 600K. The CIT experiments allow for the examination of the behavior of intermediate species over a range of reaction times at a given temperature. For each type of experiment, 15 gas samples are extracted from the reaction and rapidly quenched to stop the reaction, the intermediate species are then identified using gas chromatography, gas chromatography/mass spectroscopy (GC/MS), gas chromatography/Fourier Transform Infrared Spectroscopy (GC/FT-IR), and on-line FT-IR. Furthermore, in-situ techniques, such as Cavity Ringdown Laser Absorption Spectroscopy (CRLAS), Magneto-Optic Rotation (MOR), and Cavity Enhanced Magneto-Optic Rotation (CEMOR), were developed to permit measurements of selected stable and radical species. The results from these experimental studies are being used to develop appropriate detailed and reduced/skeletal kinetic models for the ignition and oxidation behavior of the fuels examined.

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## I. INTRODUCTION

### A. Motivation

The next generation of military vehicles will demand higher performance propulsion systems that deliver increased power, fuel efficiency, and low observable emissions. There is strong evidence that low and intermediate temperature hydrocarbon fuel chemistry controls the important preignition process through heat release and formation of reactive species. Difficulties with the preignition process can result in several significant engine problems, such as knock in spark ignition engines and misfire or cold start difficulties in diesel engines.

During the compression ignition process, a complex set of preignition reactions lead up to the point of ignition. The tendency of the fuel to react prior to the point of ignition is directly related to its chemical structure. In order to gain insight into the autoignition processes of hydrocarbon fuels, it is necessary to understand the oxidation process. A detailed understanding of this process will permit modeling of the heat release, reaction intermediates, and reaction products. During the oxidation process, large numbers of concurrent and competing reactions are occurring simultaneously and yield correspondingly large number of reaction intermediates. Even for “small” hydrocarbons such as butane, reaction models include thousands of reactions involving hundreds of species. As the size of the fuel increases, the number of reaction intermediates exponentially increases. Hence, attempting to understand the detailed chemistry of distillate fuels, which are multicomponent blends of high molecular weight hydrocarbons, from direct studies has proven to be unattainable.

One method to understand the detailed chemistry of distillate fuels is to develop an understanding of the individual constituents of the distillate fuel and simplified blends of these constituents under well controlled conditions in laboratory scale chemical reactors. Utilizing this approach, effects of different classes of hydrocarbons in distillate fuels, such as alkanes, alkenes, aromatics, and naphthenes, can be examined to understand how these classes interact and control the ignition behavior. Such studies can lead to the prediction of ignition behavior without extensive engine testing. Hence, a research program to study these interactions has been conducted at Drexel University. The program started May 1998 through a research grant from the Army Research Office (Contract No. DAAG55-98-1-0286, Project No. 37699-EG), and included efforts under an associated AASERT award (Contract No. DAAG55-97-1-0196; Project

No. 36910-EG-AAS). This final report documents the activities conducted under these programs which was completed in April 2002.

## B. Objectives

The overall objectives for this research program were to:

- obtain kinetic information in the low and intermediate temperature ranges (600 - 1000 K) over a range of pressures (up to 20 atm) for the oxidation of pure hydrocarbons with carbon numbers  $> 5$ ;
- determine the interactions controlling ignition of 2, 3 and 4 component mixtures of full boiling range fuel constituents;
- investigate the use of such mixtures as “surrogates” to represent full boiling range fuels by direct comparison with the ignition behavior of industry standard fuels; and
- develop detailed and reduced chemical mechanisms which can model the progress of these reactions over the experimental range of conditions for use in predicting ignition and emissions characteristics.

## C. Methodology

The methodology of the program was to perform bench scale tests on single and multicomponent blends of neat fuels and selected distillate and full boiling range fuels. The fuels were branched and straight chain alkanes, alkenes, aromatics, and naphthenes, which are representative of compound found in both gasoline and diesel fuels. The experiments were conducted using our pressurized flow reactor facility. This facility can examine fuels at various temperatures (600 - 1000 K) and pressures (up to 20 atm) over a range of reaction times that are representative of engine operating conditions prior to and after ignition. Several methods were employed to determine the stable intermediates of the oxidation process, namely: gas chromatography, gas chromatography with Fourier Transform Infrared Spectroscopy (GC/FT-IR), gas chromatograph with a mass selective detector (GC/MSD), and on-line FT-IR analyses. Results of these studies were used to provide kinetic and mechanistic information, to formulate hypotheses on autoignition mechanisms, to determine the effects of various functional groups within multicomponent fuels, and to validate combustion models which can be used in the design and evaluation of engines.



## II. RESEARCH PROGRAM

### A. Research Overview

This research program investigated the chemistry of high pressure oxidation and the ignition characteristics of hydrocarbon fuels. The expressed purpose of which was to develop kinetic and mechanistic information in the low and intermediate temperature regime. This was accomplished by performing experiments that oxidize single component fuels and blends of 2, 3, and 4 components. The fuels investigated consist of straight and/or branched alkanes, alkenes, aromatics, and naphthenes. Experiments were carried out in a pressurized flow reactor under conditions that simulate actual engine conditions prior to and during the ignition process. Various methods were employed to determine the stable intermediates of the oxidation process, namely: gas chromatography, gas chromatography with Fourier Transform Infrared Spectroscopy (GC/FT-IR), gas chromatograph with a mass selective detector (GC/MSD), and on-line FT-IR analyses. In addition to these techniques, in-situ laser based techniques were developed and used to determine selected radical and stable oxidation products, namely Cavity Ringdown Laser Absorption Spectroscopy (CRLAS), Magneto-Optic Rotation (MOR), and Cavity Enhanced Magneto-Optic Rotation (CEMOR). Associated in house and collaborative modeling efforts were directed towards developing detailed and reduced chemical mechanisms which can be used to model and predict relevant ignition and emissions characteristics.

### B. Specific Research Accomplishments

A number of specific research accomplishments for the current research program are identifiable. The major activities are listed below, roughly in chronological order, along with a brief discussion of their significance.

1. Developed a functional group quantification technique using Fourier Transform Infrared Spectroscopy (FT-IR).

A technique to quantify the evolution of different functional groups, namely alkanes, olefins, aromatic, and aldehydes, was developed. This technique allows for semi-qualitative analysis of complex mixtures that result from our experiments. Group analysis uses key spectral features from each functional group to quantify their

concentrations. These features included the C-H bending vibrational bands for olefins and aromatics at 900 and 700 wavenumber respectively, the C=O stretching band for aldehydes around 1700 wavenumber, and the C-H stretching band for alkanes around 3000 wavenumber. A specific order for spectral subtraction was used to eliminate overlapping spectral features.

2. Developed a simplified 4-component surrogate mixture that closely matches the reactivity of industry standard gasolines in the low and intermediate temperature regimes.

Adding a representative olefin (1-pentene) and aromatic (toluene) to a mixture of saturates (iso-octane and n-heptane) produces a simple surrogate mixture that closely follows the preignition and Negative Temperature Coefficient (NTC) behavior of full boiling range fuels. Use of such surrogates greatly simplifies collection, analysis, and interpretation of experimental data, while retaining the critical features of the underlying fuel chemistry.

3. Completed experimental neopentane oxidation studies in the Pressurized Flow Reactor (PFR).

It is generally accepted that NTC behavior occurs due to a switch in the reaction mechanism dominance from alkylperoxies to conjugate alkenes in the NTC region. Neopentane has a unique molecular structure that does not form conjugate alkenes, yet using our PFR facility, we confirmed that it indeed exhibits NTC behavior. Therefore, the traditional theory of the NTC behavior does not apply and alternative explanations must be sought. Understanding its NTC behavior significantly improves our understanding of autoignition. Detailed product distributions in low and intermediate temperature regimes, measured using FT-IR Spectroscopy and Non-Dispersive Infrared Analysis, were used for modeling purposes.

4. Completed modeling work of neopentane oxidation in the low and intermediate temperature regimes.

In conjunction with Drs. Henry Curran, William Pitz and Charles Westbrook at Lawrence Livermore National Laboratory (LLNL), an existing detailed model for neopentane oxidation was examined and refined. This model was first developed based on limited experimental results by Baker et al. (1976). After identifying some deficiencies in the existing model, several modifications were made to improve it: (1) upgrading the thermodynamic parameters of alkyl radical and alkylperoxy radical species; (2) adding an alternative isomerization reaction of hydroperoxy-neopentylperoxy; and (3) adding a multi-step reaction sequence for 2-methylpropan-2-yl radical with molecular oxygen. These changes have improved the calculation of overall reactivity. The new model can reproduce all major species profiles measured in the experiment.

5. Completed the group analyses for the oxidation of 87 PRF and 92 PRF, simple 2-component blends, in the Pressurized Flow Reactor (PFR).

Two blends, 87 PRF (blend of iso-octane and n-heptane) and 92 PRF (blend of iso-octane and n-heptane), were tested. Both blends were oxidized in the PFR at the same conditions; pressure of 8 atm, equivalence ratio of 0.3, nitrogen dilution of 62%. Using reactivity mapping of CO, NTC behavior was observed for both fuel blends. The temperature at which the reactivity peaks, referred to as the start of NTC, started at approximately the same temperature. For 87 PRF the NTC region started at 688 K, while for 92 PRF it started at 686 K.

6. Completed the group analyses for the oxidation of several Industry Standard Fuels (ISF's) and the 4-component ISF surrogate, RON 92.

Five fuels were analyzed: RFA (Auto-Oil Program Reference Fuel A), RFB (Auto-Oil Program Reference Fuel B), a standard Ford test fuel, Indolene (EPA Certification Test Fuel), and the specially developed 92 research octane blend, RON 92. All blends were oxidized in the PFR at the same conditions; a pressure of 8 atm, equivalence ratio of 0.3, nitrogen dilution of 62%. Using reactivity mapping of CO, NTC behavior was observed for all of the fuels examined. The temperature at which the reactivity peaks, referred to as the start of NTC, varied from fuel to fuel, but was notably higher than the previous 2-component blends, 87 PRF and 92 PRF. RFA, RFB, Ford fuel, and Indolene NTC behavior started at temperatures of 699 K, 703 K, 700 K, and 702 K, respectively. Furthermore, the ISF's also had a notable decrease in reactivity as compared to the PRF's. This change was related to the presence of olefins and aromatics in the fuels and this was the principal motivation for the addition of these functional groups to the RON 92 blend. As a result, the RON 92 blend also exhibited a decrease in reactivity and a shift of the NTC region to 17°C higher than was observed in the 2-component blends, 87 PRF and 92 PRF. This experiment has shown that the surrogate fuel blends can be used to study the complex interaction of ISF's components.

7. Developed a bench top facility to generate and analyze highly reactive radicals.

Since the exact lines and relative strength of most radicals have not been experimentally measured, only predicted, we have developed a system that can be used to create radicals. The current configuration has been developed to generate HO<sub>2</sub> radicals. The system generates Cl radicals which then react with H<sub>2</sub>O<sub>2</sub> to produce the HO<sub>2</sub> radical.

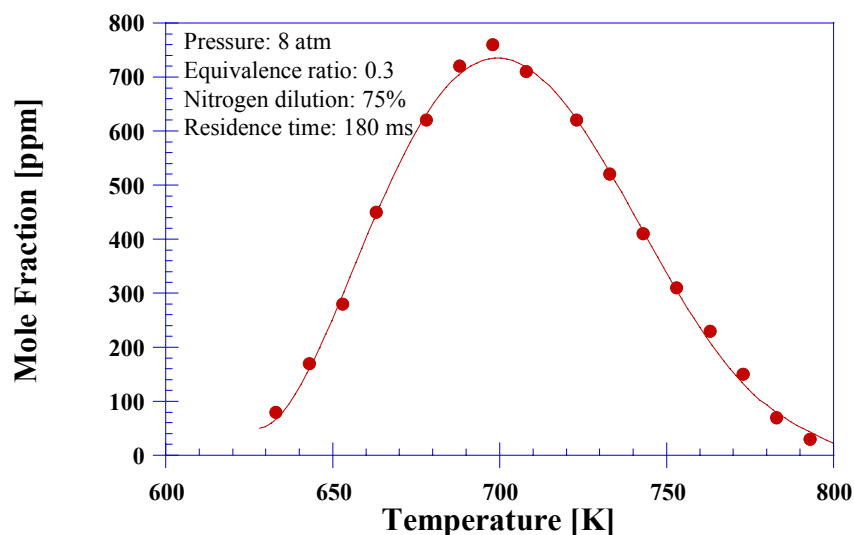
8. Developed and tested a Cavity Ringdown Laser Absorption Spectroscopy (CRLAS) system.

In developing this technique, quantitative cavity ringdown measurements of atomic calcium and gallium in an air-acetylene flame were taken and used to compare CRLAS sensitivity to that of a conventional atomic absorption (AA) setup using the same equipment. Using CRLAS detection, we observed a sensitivity increase of greater than

$10^5$  over our lower limit detectable through AA. This improvement in detection capabilities coupled with an increased dynamic range of detection should prove more than adequate for observation of highly reactive radical species. However, in the region of interest for  $\text{HO}_2$ , (around 1430 nm) there are a tremendous number of lines due to stable combustion species such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Though CRLAS has a detection limit low enough to measure  $\text{HO}_2$ , the large number of other spectral lines will make its measurement difficult. Therefore, an optical technique of “separating” the radicals from nonradicals would be very advantageous.

9. Identified the existence of a NTC region for JP-8 in the low to intermediate temperature regime.

JP-8 was oxidized in the PFR. Utilizing our carbon monoxide (CO) reactivity mapping technique, a clear NTC behavior was observed for JP-8 (Figure 1). The JP-8 experiment was conducted, at a pressure of 8 atm, equivalence ratio of 0.3, nitrogen dilution of 75%, and residence time of 180 ms. The temperature at which the reactivity peaks, referred to as the start of NTC, occurred at 700 K.

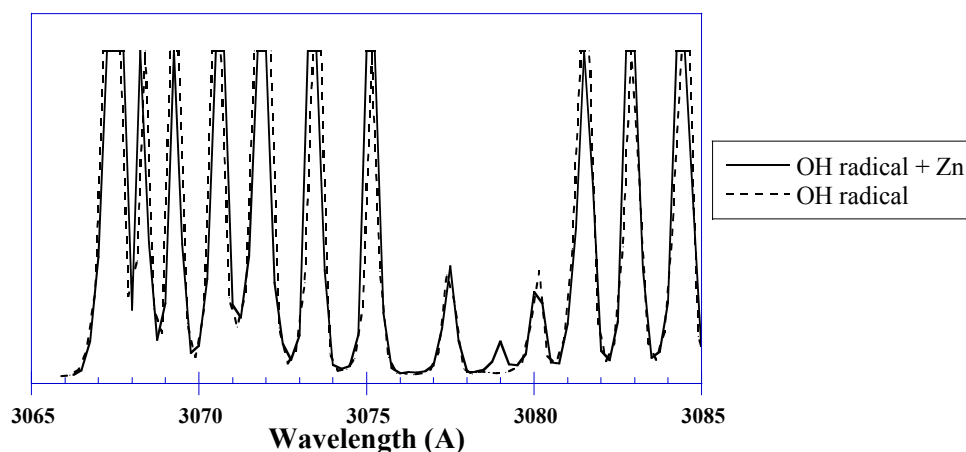


**Figure 1: Controlled cool down PFR experiment for JP-8, showing a strong NTC behavior.**

10. Developed and tested of Magneto-Optic Rotation (MOR) as a method of differentiating radicals and non-radicals with overlapping IR absorption spectra using Cavity Ringdown Laser Absorption Spectroscopy.

Preliminary measurements using the cavity ringdown technique around 1430 nm indicated that this region is much more congested spectrally than originally suspected. Therefore, finding lines due to the weakly absorbing  $\text{HO}_2$  radicals will be difficult unless the radicals are “selected” from the stable species. This selection is possible optically using a technique involving MOR. The principal of MOR uses a quantum effect known as the Faraday effect. This effect results in the ability of paramagnetic, i.e. radicals, to

rotate polarized light when exposed to a magnetic field. The degree of rotation depends on the radical concentration and the wavelength of the polarized light. Thus measuring the degree of rotation at a particular wavelength will permit the identification and quantification of a radical free from the spectral effects of non-paramagnetic species, i.e. nonradicals. An MOR experiment was performed in an acetylene/air flame that was doped with Zn atoms (which are very weakly paramagnetic). A 4 kilogauss external magnetic field was applied axially with respect to the laser propagation direction. A small nitrogen-pumped dye laser was used as the MOR source and scanned from 305 to 312 nm. The results (Figure 2) have been very encouraging. Absorption spectra without MOR show a very strong line at 307.59 nm caused by the strongly absorbing Zn atoms and 25 to 30 much weaker lines due to OH radical. With MOR, the spectrum is considerably different. The Zn line has become much weaker while the OH lines appear much stronger.



**Figure 2: Hydroxyl radical spectra with and without Zn atom doping in an acetylene/air flame, demonstrating the ability of the Magneto-Optic Rotation technique to discriminate OH from a strongly absorbing Zn atom.**

11. Developed and tested a statistical technique for the analysis of complex multi-component FT-IR spectra.

For larger hydrocarbons ( $C > 5$ ) and multi-component blends, the number of intermediate species becomes sufficiently large that direct analysis of FT-IR spectra becomes unrealistic. Chemometrics offers a statistical approach to species identification and concentration measurements. Two chemometric techniques, factor analysis and target testing, have been applied thus far. Factor analysis is a method by which the number of independent chemical species affecting the FT-IR absorption spectra of a multi-component mixture can be determined. Target testing is a method that tests whether a single chemical species has affected the measured multi-component spectra. Utilizing MATLAB and some general factor analysis and target testing algorithms, testing began into its capability to correctly determine the number and the identity of chemical species in a mixture. After development, neopentane oxidation data was analyzed with the enhanced code; the results identified nine different chemical species.

This result is the same as the number of species identified during previous research. Furthermore, the method was able to identify all but one of the species identified previously.

12. Refined the sensitivity and selectivity of Magneto-Optic Rotation (MOR).

Refining the MOR technique, we conducted experiments investigating concentration and experimental configuration effects on MOR with two weakly paramagnetic species, gallium and calcium, seeded into an air-acetylene flame. We observed absorption and MOR spectra of both calcium and gallium and determined sensitivity limits and optimal laser configuration. Lower detection limits were approximately 40 ppm and 50 ppb for gallium and calcium, respectively. Next, we investigated the absorption and MOR spectra of tellurium (Te) isotope 130, a non-paramagnetic species, and calcium (Ca) in the blue region of the visible spectrum (420-425 nm). While detection of the Ca absorption line among the Te lines was very difficult using standard absorption techniques, MOR enabled selective observation of the weakly paramagnetic calcium. The MOR technique greatly expanded our ability to identify radical species in regions of the electromagnetic spectrum congested by multiple stable species with multiple lines by virtually eliminating the signals from these species.

13. Upgraded the liquid fuel delivery system for the pressurized flow reactor facility.

Due to the high reactivity of diesel type compounds, low fuel concentrations were necessary, thus the injection of very low liquid flow rates into the PFR had to be controlled. The existing method wasn't stable enough to consistently deliver the low flow rates, as a result, the fuel delivery system was updated with a high pressure syringe pump capable of delivering flow rates between 0 to 200 ml/min in 0.001 ml/min increments. This new delivery method has greatly increased system repeatability (CO mapping differences less than 5%) and decreased concentration variations during CIT and CCD experiments.

14. Identified the major intermediate oxidation species for n-heptane, iso-octane, 1-pentene and the 4-component ISF surrogate, RON 92.

Each of RON 92's components (n-heptane, iso-octane, 1-pentene, and toluene) and the entire mixture were oxidized in Drexel University's Pressurized Flow Reactor (PFR), in order to obtain reactivity maps and species profile information. Representative reactivity mapping data are shown in Figure 3, which clearly shows the start, stop, and peak of reactivity for each fuel. For each experiment 15 gas samples were extracted from the reaction and rapidly quenched to stop the reaction, the intermediate species are then identified using a Gas Chromatograph coupled to a Mass Spectrometer or quantified using a Gas Chromatograph with a Flame Ionization Detector. Currently, identification of the major intermediate species has been completed for each of the individual components and their mixtures, and species quantification is underway.

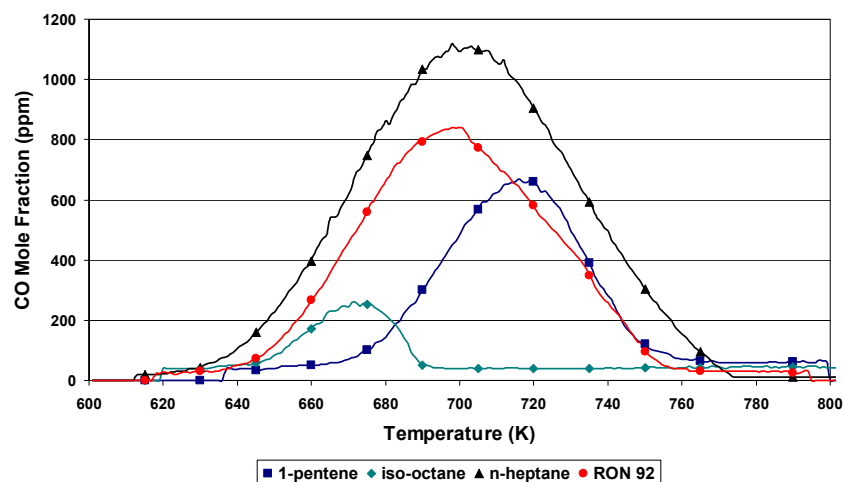


Figure 3: Reactivity map of RON 92 and its components.

15. Established the potential of Cavity Enhanced Magneto-Optical Rotation (CEMOR) as a viable diagnostic technique.

We tested the CEMOR concept and characterized the interactions between MOR and CRLAS utilizing gallium in an air-acetylene flame. These “proof of concept” experiments successfully demonstrated that CEMOR works and indicated that CEMOR has potential for the selective detection of radical species. In experiments spanning a range of gallium concentrations, we observed that the time to the maximum signal occurs earlier for higher concentrations. These initial observations indicate that the time associated with this maximum could be used to determine concentration. CEMOR is very promising for the study of radical species, as it allows the selective detection of trace quantities of these using IR regions with multiple absorbers.

16. Upgraded our dye laser system to a Nd:YAG pumped Optical Parametric Oscillator (OPO) laser system.

With funding from the DOD DURIP program (DAAD19-01-1-0438), we purchased a Nd:YAG pumped Optical Parametric Oscillator (OPO) laser system with a frequency doubler. The OPO is a solid state alternative to a dye laser system, and is continuously tunable from the UV (220 nm) to the near IR (1700 nm). This equipment will facilitate our optical diagnostic activities.

17. Identified the existence of a NTC region for the neat distillate fuel components n-dodecane, isocetane, methylcyclohexane, decalin,  $\alpha$ -methylnaphthalene, and hexylbenzene in the low to intermediate temperature regime.

Using the CO reactivity mapping technique, the oxidation of neat n-dodecane, isocetane, methylcyclohexane, decalin,  $\alpha$ -methylnaphthalene, and hexylbenzene was

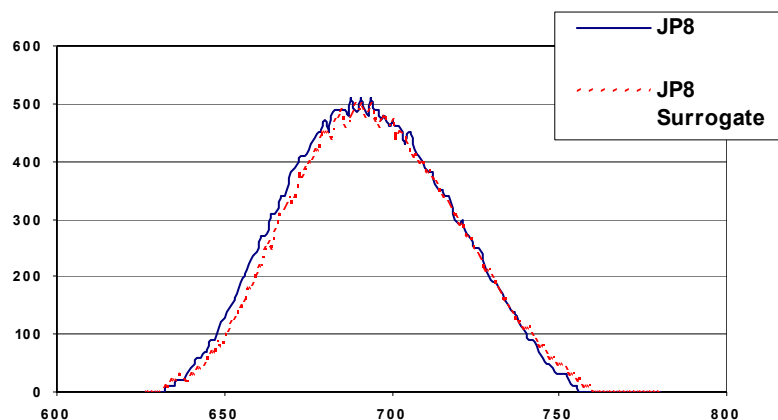
examined. Both n-dodecane and decalin showed strong NTC behavior starting at 700K and 695K, respectively, over all the conditions tested. However decalin reacted over a very narrow temperature range, approximately between 725K and 655K, compared to the corresponding values for n-dodecane, 800K and 600K. Methylcyclohexane did not oxidize at lean conditions (equivalence ratio  $\Phi = 0.30$ , N<sub>2</sub> dilution = 80%), while it became unstable and explosive at richer conditions ( $\Phi = 0.70$ , N<sub>2</sub> dilution = 65%). Controlled oxidation of methylcyclohexane was not achievable in our system due to its high resistance to oxidation and very high energy density. The other pure hydrocarbons tested, (the aromatics and isocetane) were resistant to ignition, and no reactivity was observed for the conditions tested.

18. Developed a simplified 5-component surrogate mixture that closely matches the reactivity of JP-8 in the low and intermediate temperature regimes.

Building upon the single component distillate fuel work, blends of binary, ternary, and larger mixtures were used to develop a simplified surrogate for JP-8. All mixtures were prepared with a cetane number of approximately 45, and they were oxidized at 8 atm, equivalence ratio of 0.30, nitrogen dilution of 80%, and residence time of 120 ms. A total of 3 binary, 2 ternary, and 6 larger mixtures were oxidized over a temperature range of 800K to 600K and compared with the CO reactivity map of JP-8. All components, except methylcyclohexane, were blended together assuming linear blending. Methylcyclohexane behaved as if it was more reactive than the corresponding ideal linear blend and, as a result, a blended cetane number was determined using a linear correlation between the maximum CO production and the fuel (or mixture) cetane number. This correlation was developed and tested using the data obtained from the oxidation of both the pure hydrocarbons and binary mixtures.

Several criteria were used to determine the ability of each surrogate to match the reactivity map of JP-8. The criteria included: the start and stop of reactivity, the start of the NTC region, the magnitude of overall reactivity, and a composition that matched JP-8's published values. Upon analysis of the above mixtures, the mixture that matched the JP-8 reactivity the closest was a five component mixture consisting of 26% n-dodecane, 36% isocetane, 14% methylcyclohexane, 6% decalin, and 18%  $\alpha$ -methylnaphthalene. The reactivity map of this mixture and that of JP-8 is shown below.

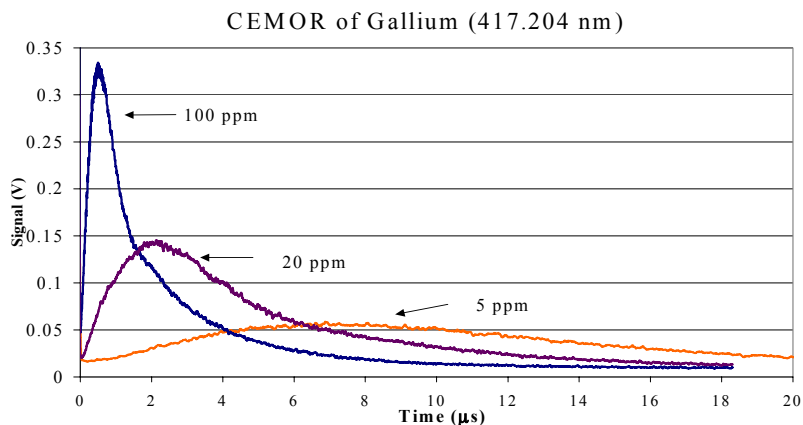




**Figure 4: CO reactivity map of JP-8 and its surrogate (26% n-dodecane, 36% isocetane, 14% methylcyclohexane, 6% decalin, and 18%  $\alpha$ -methylnaphthalene).**

#### 19. Development and testing of Cavity Enhanced Magneto-Optical Rotation (CEMOR).

Due the promising nature of CEMOR, additional research was conducted to make it a viable combustion diagnostic technique. First, the temporal behavior of CEMOR was examined, and the results are illustrated in Figure 5. The maximum intensity of CEMOR signals is proportional to sample concentration, as theoretically predicted by the quadratic dependence of transmitted intensity on number density. Interestingly, the time to reach the peak signal intensity depends inversely on number density because less per pass rotation is experienced at lower concentrations. At higher concentrations the time to reach maximum rotation signal, “build-up time”, is dependent on sample concentration. At low concentrations (below 2 ppm) the build-up times for different number densities become indistinguishable. CEMOR will thus permit identification and quantification of radical species in crowded spectral regions. Currently, we are using this system to study OH radical spectra in a flame in the 1380-1410 nm region with new Nd:YAG pumped Optical Parametric Oscillator (OPO). We have also filed for a provisional patent on the CEMOR technique.



**Figure 5: Effects of concentration on the CEMOR signal.**

### C. Reports, Publications, and Presentations

Work accomplished as part of this research program has contributed to and resulted in the following reports, publications, and presentations:

Wang, S., Khan, A. R., Miller, D. L., and Cernansky, N. P. (1998): "Neopentane Oxidation in the Low and Intermediate Temperature Regime and at Elevated Pressure (8 atm)." Paper No. WSSCI 98S-61, presented at the Spring Meeting of the Western States Section of the Combustion Institute, University of California, Berkeley, CA, March.

Khan, A. R. (1998): "Oxidation of Industry Standard Fuels and Blends of Primary Reference Fuels in the Low Temperature and Negative Temperature Coefficient Regions", Masters Thesis, Drexel University, Philadelphia, PA.

Billmers, R. I., Aniolek, K. W., Cernansky, N. P., and Miller, D. L. (1999): "Detection of Polyatomic Molecules and Radicals in Combustion Environments Using Cavity Ringdown Laser Absorption Spectroscopy", Paper No. 1075, presented at The Pittsburgh Conference 1999, Orlando Convention Center, Session Name: "Analytical Solutions to Problems in Fuels and Power Systems".

Wang, S. (1999): "Experimental and Modeling Study of Preignition Chemistry of Hydrocarbons", Ph.D. Thesis, Drexel University, Philadelphia, PA.

Wang, S., Miller, D. L., Cernansky, N. P., Curran, H. J., Pitz, W. J., and Westbrook, C. K. (1999): "A Flow Reactor Study of Neopentane Oxidation at 8 Atmospheres: Experimental and Modeling", *Combustion and Flame*, Vol 118, pp. 415-430.

Lenhert, D. B., Billmers, R. I., Cernansky, N. P., and Miller, D. L. (2000): "Determination of Partial Oxidation Products in a Pressurized Flow Reactor System using FTIR Spectroscopy with Chemometrics", Paper No. 708, presented at The Pittsburgh Conference 2000, New Orleans Convention Center, Session Name: "Chemometrics III".

Billmers, R. I., Emig, M. F., Cernansky, N. P., and Miller, D. L. (2001): "Cavity enhanced magneto-optic rotation: a very sensitive and selective technique of detecting paramagnetic species", Paper No. 708, presented at the Conference on Lasers and Electro-Optics 2001, Baltimore Convention Center, Session Name: "Optical Instrumentation and Measurements II", May 10, 2001.

Zheng, J., Miller, D.L., and Cernansky, N.P., "Predicting Preignition Reactivity of Real Fuels Using Skeletal Kinetic Models", prepared for an NSF Workshop on New Combustion Models with Practical Fuels, S. Margherita Ligure, Italy, 20 September 2001: also Paper No. ESSCI 2001-062, presented at the Eastern States Section Combustion Institute Meeting, Hilton Head, South Carolina, 3-5 December 2001.

Emig, M., Miller, D. L., Billmers, R. I., Cernansky, N. P., and Owens, K. G. (2001): "Cavity Enhanced Magneto-Optic Rotation: A Sensitive and Selective Technique for Detection of Paramagnetic Species", Paper No. ESSCI 2002-101, presented at the Eastern States Section of the Combustion Institute Meeting, Hilton Head, South Carolina, 3-5 December 2001

Zheng, J., Yang, W., Miller, D.L., and Cernansky, N.P., "A Global Reaction Model for the HCCI Combustion Process", Paper No. WSSCI 2-02S-064, presented at the Western States Section of the Combustion Institute, San Diego, California, 25-26 March 2002.

Emig, M., Billmers, R. I., Cernansky, N. P., Miller, D. L., and Owens, K. G. (2002): "Cavity Enhanced Magneto-Optic Rotation Spectroscopy of Combustion Generated Radicals", presented at the Conference on Lasers and Electro-Optics 2002, Long Beach Convention Center, Session Name: "Laser-Based Gas and Chemical Sensing", May 24, 2002.

Agosta, A. (2002): "Development of a Chemical Surrogate for JP-8 Aviation Fuel Using a Pressurized Flow Reactor", Masters Thesis, Drexel University, Philadelphia, PA.

Emig, M. Billmers R. I., Owens, K. G., Cernansky, N. P., Miller, D. L., and Narducci, F. A. (2002): "Sensitive and Selective Detection of Paramagnetic Species Using Cavity Enhanced Magneto-Optic Rotation", Applied Spectroscopy, in press.

Note: The Masters Thesis of D.B. Lenhart and publications associated with the Agosta and Lenhart theses are expected later this summer.

#### D. Research Personnel and Activities

This research program was coordinated under the supervision of Dr. Nicholas P. Cernansky and Dr. David L. Miller as Co-Principal Investigators. They shared overall responsibility for conducting, directing, and reporting various phases of this research program. However, the primary responsibility for carrying out and implementing the details of the experimental and analytical aspects of the program fell on the graduate students and technical personnel supported by the project.

N. P. Cernansky - Co-Principal Investigator  
D. L. Miller - Co-Principal Investigator  
R. L. Billmers - Research Associate Professor, Ph.D.

#### LIST OF SUPPORTED GRADUATE STUDENTS

A. Khan - Research Assistant, M.S. (August 1998)  
S. Wang - Research Assistant, Ph.D. (May 1999)  
B. Brook - Research Assistant, Ph.D. (departed May 2000)  
M. F. Emig - Research Assistant, B.S. (June 2002)  
A. Agosta - Research Assistant, M.S. (June 2002)  
D. B. Lenhart - Research Assistant, M.S./Ph.D. (M.S. expected August 2002)

#### F. Report of Inventions

##### CEMOR Patent

“Cavity Enhanced Magneto-Optic Rotation Spectroscopy and Uses Thereof”,  
U.S. Provisional Patent Application, filed 9 May 2002.